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National Environmental Testing

Dayton Division

Standard Operating Procedure

Analyte or Suite: GFAA Aqueous Sample Preparation

Methodology: Acid Digestion Procedure for GFAA

Reference: Method 3020A, SW-846, 3rd Edition

Revision: # 1 Date revised: 17 September 96

File Name: /usr3/sops/MET/S-3020A.GFAA

Approvals:

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1. INTRODUCTION AND SCOPE

1.1. General

Preservation: HNO3 to pH <2, Cool - 4Q C

Container: 500cc plastic, glass is also acceptable

Minimum sample volume: 50 mL for a single digestion

Holding Time: 6 months

Method No.(s) and References:
3020, SW-846, 3rd Edition
Metals Section 4.1.3, EPA 600/4-79-020, Revised March 1983

1.2. This method is an acid digestion procedure used to prepare aqueous samples, TCLP, EPTOX, and mobility-procedure extracts, and wastes that contain suspended solids for the analysis by graphite furnace atomic absorption spectroscopy.

1.3. Samples prepared by this method may be analyzed by GFAA for the following metals:

Arsenic	Molybdenum
Beryllium	Selenium
Cadmium	Silver
Chromium	Thallium
Cobalt	Vanadium
Lead	

It is possible to use this method as a preparation procedure for other elements not specifically listed. If this is the case, the Quality Control Indicators (QCI) should be closely evaluated to determine this method's applicability. Refer to Section 11. Summary of Modifications/Method Comparision for additional discussion.

1.4. Your ability to follow this method according to the specifications herein will affect your performance evaluations, the quality of data produced for this application, your section's productivity, and the laboratory's profitability.

2. SUMMARY OF METHOD

A mixture of HNO3 and the material to be analyzed is refluxed in a Griffin beaker until until the digestate is light in color or until its color has stabilized. After the digestate has been

brought to a low volume, it is cooled and brought up to volume in dilute nitric acid.

3. SAFETY

Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures PRIOR TO THE USE of any chemical. In all cases, both the applicable MSDS and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the NET Safety Manual. The bottle labels also provide important information that must be noted. Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much care as any of the materials used in this method due to the unknown nature of their composition.

4. REAGENTS AND MATERIALS

4.1. Apparatus.

4.1.1. Hot Plate

4.1.2. 150 mL beakers, VWR Catalogue No. 13912-182 or other appropriate vessels such as erlenmeyer flasks.

4.2. Reagents.

All reagents must be properly labelled with the reagent identification and concentration, date prepared, expiration date, initials of analyst, and applicable safety information. Labels are available through the centralized purchasing system. The label has a place for the NFPA diamond, which will be used to indicate health (blue), flammability (red), reactivity (yellow), and contact/special (white) information obtained from applicable Material Safety Data Sheets (MSDS) supplied by the vendor.

4.2.1. Deionized water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent

source. Use deionized water for the preparation of all reagents, standards, and dilution water.

4.2.2. Concentrated Nitric Acid, VWR Catalogue No. JT9601-33. If metal impurities are found to be present, use a spectrograde acid.

HNO3
NFPA diamond: health = 3, flammability = 0, reactivity = 3, contact = 4.

Strong oxidizer. Contact with other material may cause fire. Liquid and vapor cause severe burns. May be fatal if swallowed. Harmful if inhaled and may cause delayed lung injury. Keep from contact with clothing and other combustible materials. Do not get in eyes, on skin.

4.3. Standards.

See the appropriate analytical SOP for details.

5. INTERFERENCES

5.1. Interferences are discussed in the analytical SOPs.

6. ANALYTICAL PROCEDURES

6.1. Preservation and Handling.

6.1.1. For the detemination of acid-soluble metals, contamination and loss are of prime concnern. Dust in the laboratory environment, impurities in reagents and improperly cleaned laboratory apparatus which the sample contacts are all potential sources of contamination. Sample containers can introduce either positive or negative errors in the measurement of metals by (a) contributing contaminants through leaching or surface desorption and/or (b) by depleting concentration through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program should document through the use of spiked samples, reagent and sample blanks, that cleaning procedures are adequate. Before collection of the sample a decision must be made as to the type of data desired, ie., dissolved, suspended, or total.

6.1.2. All metals samples (except Cr VI) must be acidified to a pH < 2 with nitric acid upon collection, except samples which

need to be filtered at the laboratory. Ideally, samples requiring filtration should be filtered in the field. Mercury analyses must be conducted within 28 days; other metals analyses have a holding time of six months.

6.1.3. For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. A glass fiber pre-filter may be used in combination with the 0.45 u membrane filter. Glass or plastic filtering apparatus using membrane filters are recommended to avoid possible contamination. Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 HNO3 to a pH of <2. Normally, 2-3 ml of (1:1) acid per liter should be sufficient to preserve the sample. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

6.2. Glassware Preparation.

6.2.1. All glassware for metals analysis will be kept separate and labelled for metal analysis only.

6.3. Sample Analysis.

6.3.1. Transfer a 50 to 100-mL representative aliquot of the well mixed sample to a 150-mL Griffin beaker. Choose a volume of sample appropriate for the expected concentration. of metals. The sample volume required may vary proportionally with the number of metals to be determined. Add 3 mL of concentrated HNO_3. (For As and Se add an additional 2mL of 30% hydrogen peroxide.) Place the beaker on a hot plate and cautiously evaporate to the lowest reasonable volume, making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker.

Note: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

6.3.2. If necessary, continue heating, adding additional acid until the digestion is complete. Generally, this is indicated when the digestate is light in color or does not change in appearance with continued refluxing. Add a small quantity of deionized water, approximately 10 mL, and warm the beaker for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

6.3.3. After cooling, dilute to final volume with DI water using

a volumetric flask.

6.3.4. If plating out of AgCl is suspected, the sample will be redigested at a dilution at which no precipitates are observed.

6.4. Calculation.

6.4.1. The concentrations determined in the digest are to be reported based on the following calculation:

$$\text{Concentration mg/L} = \frac{C \times Vf}{Vi}$$

where: C = Instrument response, (mg/L)
Vf = Final volume (mL) of digested sample
Vi = Initial volume (mL) of sample

Additional dilutions made at the time of analysis should also be included in the calculation.

7. Quality Control.

7.1. Method Performance.

7.1.1. Calibration Curve.

Not Applicable

7.1.2. Initial Calibration Verification Standard (ICVS).

Not Applicable

7.1.3. Reagent Blank (RB).

Not Applicable

7.1.4. Continuing Calibration Verification Standard (CCVS).

Not Applicable

7.1.5. Procedure Blank (PB).

The procedure blank is a deionized water blank that is subjected to the same conditions that a prepared sample undergoes. Preparation includes digestion. Analyze a minimum of one procedure blank per batch. A batch shall contain twenty samples or less. Interim acceptance criteria requires the procedure blank to be less than the reporting limit. Statistical warning

limits require the procedure blank to be within ± two standard deviations of the mean from a data base of 20 points. Statistical control limits require the blank to be less than the reporting limit. Procedure blanks are not routinely subtracted from the analytical results. Enter the procedure blank result into LABSYS II.

NOTE: If you have performed a dilution on the sample and need to assess the procedure blank, be sure to evaluate the result obtained from the analysis of the procedure blank at the same dilution.

7.1.6. Lab Control Standard (LCS).

The lab control standard is a high standard that is subjected to the same conditions that a prepared sample undergoes. Preparation includes digestion. Analyze a minimum of one LCS per batch. A batch shall contain twenty samples or less. Interim acceptance criteria requires the LCS to be within 80-120% of the true value. Statistical acceptance criteria require the LCS to be within ± three standard deviations of the mean from a data base of 20 points. Enter the LCS result into LABSYS II.

7.1.7. Matrix Spike / Matrix Spike Duplicate (MS/MSD).

The matrix spike / matrix spike duplicate pair are two separate aliquots of sample which are spiked with known concentrations of analyte and subjected to the same conditions that a sample undergoes. The spike concentration should be 20% of the top standard or equal the CLP spike guidelines. Analyze a minimum of one MS/MSD pair per every analytical batch per matrix; the two matrices monitored are water and other ie. soils and other solids and an anlytical batch is twenty samples or less. Advisory interim acceptance criteria requires the MS/MSD percent recovery to be within 75-125% and the relative percent difference to be less than 20. Advisory statistical warning limits require the MS/MSD percent recovery and RPD to be within ± two standard deviations of the mean from a data base of 20 points. Advisory statistical control limits require the MS/MSD percent recovery and RPD to be within ± three standard deviations of the mean from a data base of 20 points. The data generated can be presented, if necessary, as a statement of precision and accuracy for a particular analysis on a given matrix. Enter the MS/MSD results into LABSYS II.

7.2. Corrective Action.

If any of the method performance criteria outlined above cannot

be met, notify your supervisor immediately.

7.3. Documentation.

All quality control data should be maintained and available for easy reference and inspection.

7.4. Analyst Certification.

7.4.1. Initial Certification.

Each analyst performing this method must successfully complete three PE samples, which are administered by the QC Coordinator, one near the reporting limit, one near the middle of the curve, and one which exceeds the linear range of the curve. The SOP self test needs to be taken and reviewed with the analysts supervisor.

7.4.2. Continued Certification.

Each analyst performing this method must successfully complete at least 1 ITP sample during a 12 month period.

7.5. Method Detection Limits and Reporting Limits.

Not Applicable

8. REFERENCES

8.1. Methods for Chemical Analysis of Water and Wastes, USEPA, Environmental Monitoring and Support Laboratory EPA-600/4-79-020

8.2. Standard Methods For the Examination of Water and Wastewater, 17th Edition, APHA

8.3. Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976)

9.0 DAILY ANALYTICAL SEQUENCE

1. Procedure Blank (PB): < Reporting Limit, 1 per batch - a batch shall be 20 samples or less.
2. Lab Control Standard (LCS): 80-120% of the true value or within the statistically established range, 1 per batch - a batch shall be 20 samples or less.
3. Matrix Spike/Matrix Spike Duplicate (MS/MSD): 1 per batch - a batch shall be 20 samples or less.
4. Samples 1 - 20
5. Return to #1 if additional samples will be processed.

10. TIPS AND HINTS

It is important that feedback of QC analytical results be provided by the analytical team to the digestion team.

Metals Digestion for Aqueous Samples and Extracts for GFAA

11. Summary of Modifications / Method Comparison

Primary reference: SW-846, 3rd Edition, Method no. 3020
Secondary reference: EPA-600/4-79-020, Method no. Metals - Section 4.1.3.

EPA-600/4-79-020	Standard Methods 17th Ed.	SW-846	SOP	SOP Section Ref.
Does not specify the elements which can be analyzed by GFAA.	Same as EPA-600/4-79-020	Lists 8 elements which can be analyzed by GFAA. Does not address any additional elements. Does not include Arsenic and Selenium.	Same as SW-846 except that the following has been added: It is possible to use this method as a preparation procedure for other elements and matrices not specifically listed. The Quality Control Indicators should be closely evaluated to determine this method's applicability. List does include Arsenic and Selenium.	1.3.
Allows the choice of a volume of sample appropriate for the expected level of metals and/or the number of metals to be determined.	Same as EPA-600/4-79-020	Transfer a 100 mL representative aliquot....	Same as EPA 600/4-79-020	6.3.1.
Add 3 mL conc. HNO_3, evaporate, add another 3 mL portion of HNO_3.	Add 5 mL conc. HNO_3, evaporate, add additional portions of HNO_3 if necessary.	Same as EPA-600/4-79-020	Add HNO_3 all at one time.	6.3.1.
Final evaporation is to near dryness	Evaporate to the lowest volume possible - about 10 to 20 mL	Evaporate to low volume (3 mL), do not allow any portion of the beaker bottom to go dry.	Does not define low volume. States "evaporate to the lowest reasonable volume." Precipitation of dissolved solids during the evaporation of the sample may prevent taking the sample down	6.3. end note

Note: The Quality Control guidelines outlined in SW-846 are met with this SOP
The Quality Control guidelines outlined in EPA 600/4-79-020 are met with this SOP except for the following: Section 10.3 Optional Requiments, "At least one duplicate sample should be run every 10 samples, or with each set of samples to verify precision of the method. Checks should be within the control limits established by EPA."

DISCUSSION:

Silver: SW-846 contains the following note, "For the digestion and GFAA analysis of silver, see Method 7761." The sample preparation listed in this procedure is the same as 3020. The following additional section is included in method 7761:

> 7.3. If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyangogen iodide to the sample. This can be done only after digestion and after neutralization of the sample to a pH of >7 to prevent formation of toxic cyanide under acid conditions. In this case, do not adjust the sample volume to the predeterminied value until the sample ;has been neutralized to pH >7 and cyanogen iodide has been added. If cyangogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. Cyanogen iodide must not be added to the acidified silver standards. New standards must be made, as directed in Step 5.2., except that the acid addition step must be omitted. for example, to obtain a 100 mg/L working standard, transfer 10 mL of stock solution to a small beaker. Add water to make about 70 mL. Make the solution basic (pH avove 7) with NH4OH. Rinse the pH meter electrodes into the solution with water. Add 1 mL cyanogen iodide and allow to stand 1 hour. Transfer quantitatively to a 100 mL volumetric flask and bring to volume with water. CAUTION: CNI reagent can be added only after digestion to prevent formation of toxic cyanide under acidic conditions. CNI reagent must not be added to the acidified silver standards. NOTE: Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided.

Questions: The statement, "If plating out of AgCl is suspected.....", is pretty vague. How is it actually determined that this prep should be utilized?

This sample preparation is listed within EPA 600/4-79-020, Method 272.1 and has been commonly associated with the analysis of silver in photographic solutions. If this procedure is used, a separate preparation should not need to be performed for silver only. Rather, a 10 mL sample aliquot should be withdrawn from the total metals sample preparation (3020). A predetermined volume of NH4OH should be added to all samples, blanks, and standards consistently. Add 0.1 mL cyanogen iodide and allow to stand 1 hour.

Arsenic and Selenium:

SW-846 contains the following note, "For the digestion and GFAA analysis of arsenic and selenium, see Methods, 3050, 7060, and 7740."
The sample preparation procedure listed in each method is the same. It is as follows:

> 7.1.1. Transfer 100 mL of well-mixed sample to a 250 mL Griffin beaker; add 2 mL of 30% H2O2 and sufficient concentrated HNO3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95 C or until the volume is slightly less than 50 mL. 7.1.2. Cool and bring back to 50 mL with Type II water. 7.1.3. Pipet 5 mL of this digested solution into a 10 mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and

dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

EPA-600/4-79-020 contains similar information within the actual procedures 206.2 and 270.2.
Standard methods also contains similar information.
USEPA CLP 6/89 SOW does not use method 3020 for the preparation of aqueous samples for GFAA analyses. The SOW lists the use of the above procedure for all GFAA analytes.

General: EPA/4-79-020, Section 1.1 states, "While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment."

Standard Methods, 17th Edition, 3030A states, "Samples containing particulates or organic material generally require pretreatment before analysis. "Total metals" includes all metals, inorganically and organically bound, both dissolved and particulate. Colorless, transparent samples (primarily drinking water) containing a turbidity of <1 NTU, no odor, and single phase may be analyzed directly by atomic absorption spectroscopy for total metals without digestion."

Dayton Division Specific Appendix

Item: 1.3. Samples prepared for this method may be analyzed by GFAA for the following metals:

In addition to the metals listed in the SOP the following may be analyzed by GFAA: Silver, Nickel.

Item: 2. Summary of Method.

The beakers are not covered during the digestion period.

Item: 4.2.2. Concentrated Nitric Acid...

Ultra-pure grade concentrated nitric acid is used - VWR catalogue no. 00630

Item: 6.2.2. After washing, all glassware...

The Dayton specific glassware washing procedure has been presented in the following.

BEAKERS
1. Wash with soft cloth and hot, water.
2. Wash in dishwasher.
3. Bake 30 minutes.

GRADUATED CYLINDERS AND FILTERING APPARATUS
1. Rinse with 1% nitric acid (minimum of 3 times).
2. Rinse with DI (minimum of 3 times).

VOLUMETRIC FLASKS
Between uses:
1. Rinse with 1% nitric acid (minimum of 3 times).
2. Rinse with DI (minimum of 3 times).

End of Day:
All volumetric flasks will be soaked overnight with 1% nitric acid.

Item: 6.3.1. Mix the sample...

A 50 mL volume of well mixed sample is digested by placing the sample volume plus 3.0 mL of concentrated nitric acid into a beaker and heating on a hot plate. The sample is evaporated to a low volume (20 mL) and allowed to cool. Continue adding additional acid as necessary, until the digestion is complete. (Note: Do not add more than 7.5 mL of nitric acid total. If further additions of nitric acid are indicated, the digestion

procedure should be repeated using a smaller aliquot.)

When Digestion is complete, evaporate to a low volume (20 mL), add 10 mL of deionized water, and warm the sample for 10-15 min. Remove the sample from the hot plate and wash down the beaker while transferring into a 50 mL volumetric flask. Adjust the final volume to 50 mL using deionized water.

Item: 7.1.6. Lab Control Standard (LCS).

Presented in the following are the solutions prepared for use as LCS and spiking solutions.

FURNACE MULTI-ELEMENT SPIKING & DIGESTED STANDARD

Note: All standards are prepared in 6% Nitric Acid.

Use 2 mL of the GFAA Working Stock Standard solution for each 50 mL of sample.

ELEMENT	CONCENTRATION SPIKING SOL. (mg/L)	CONCENTRATION FINAL (mg/L)
Cr	0.20	0.008
Co	0.50	0.020
Pb	1.0	0.040
Tl	1.0	0.040
Cd	0.050	0.0020
Be	0.050	0.0020
As	1.0	0.040
Se	1.0	0.040
Ag	0.10	0.0040

Item: 7.1.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The MS/MSD spiking solutions are the same as the LCS spiking solutions see 7.1.6.

Item: 7.3. Documentation.

Verification of Data

All analytical data will be verified for completeness of QCI requirements, and will be spot checked for correct calculations. This verification will be performed by a competent analyst or the area supervisor.

After an analyst completes training on a parameter, passes a PE analysis, and demonstrates good data production for 90 days, he/she will be permitted to perform self verification of data using the form labeled as Attachment 1.

Specific documentation that needs to be completed:

Area to Document	Frequency	Acceptance Criteria
Standard/Reagent Log Book	upon opening bottle	NA
	whenever a spk soln. is made	NA
Auto pipette	monthly	+/- 4 %

Item: 7.4.1. Initial Certification.

Currently no self test is available.

Item: 10. Tips and Hints.

METALS PREPARATION CHECK LIST

DAILY

1. Empty water bottles - refill at beginning of day.
2. Empty Ultra-pure HNO3 - refill at beginning of day.
3. Empty 1:1 HCl - refill at beginning of day.
4. Pull hood doors down, turn exhaust fans off, turn light off, and check that all hot plates are turned off or unplugged.
5. Place dirty glassware in glass cleaning area.
6. Fill dilution volumetric flasks with 1% for soaking over night.
7. Check the expiration dates of spiking solutions and remake when dates indicate.
8. Put the samples on the shelves that have already been set up.
9. Clean out hoods as needed.

WEEKLY

1. Replace paper on counters.